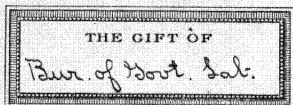
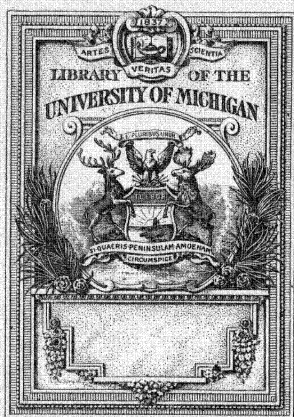


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DEPARTMENT OF THE INTERIOR
BUREAU OF GOVERNMENT LABORATORIES
CHEMICAL LABORATORY

I. AUTOCATALYTIC DECOMPOSITION OF
SILVER OXIDE
II. HYDRATION IN SOLUTION

BY
GILBERT N. LEWIS, PH. D.

MANILA
BUREAU OF PUBLIC PRINTING
1905

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(Continued on third page of cover.)

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LETTER OF TRANSMITTAL.

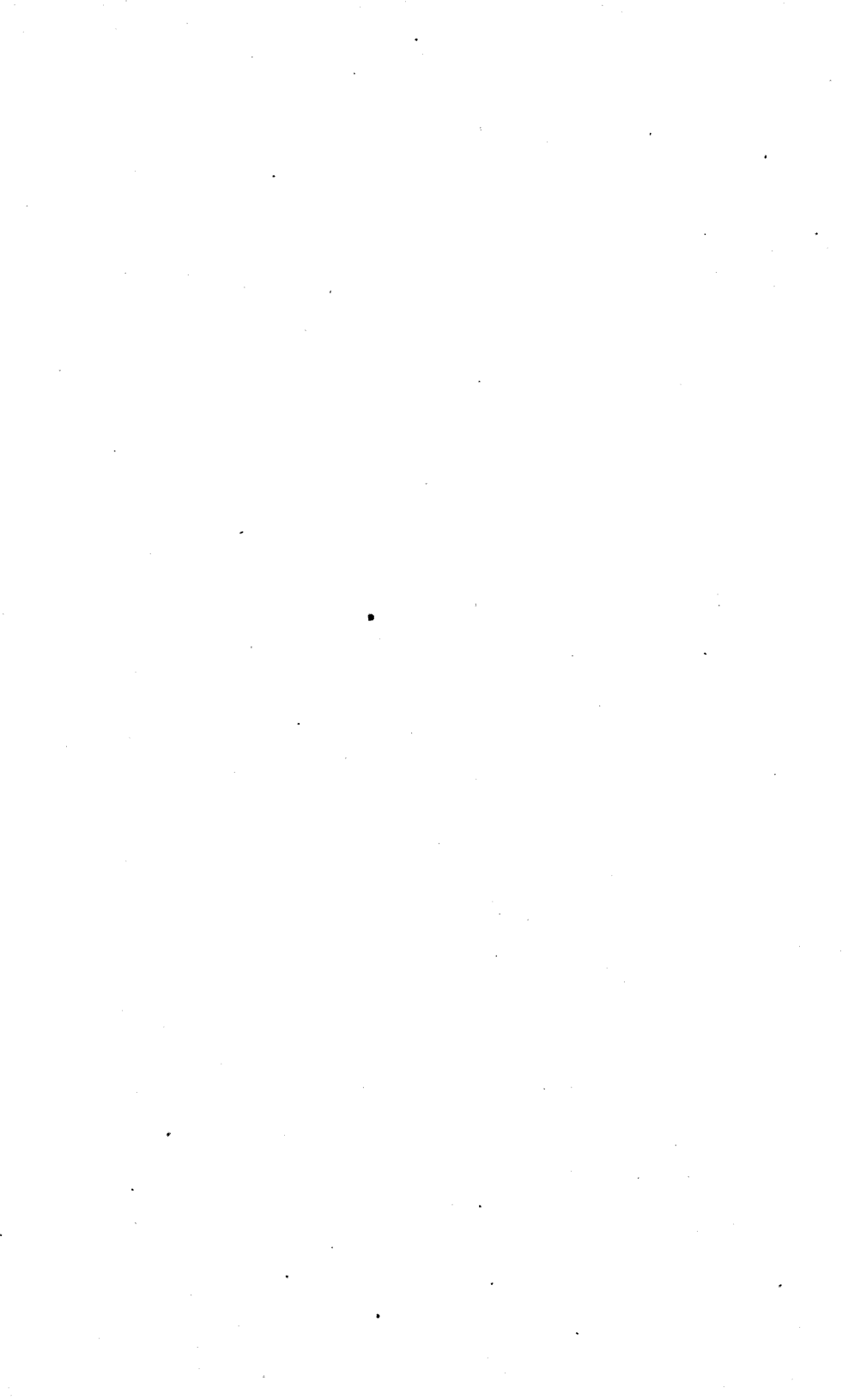
DEPARTMENT OF THE INTERIOR,
BUREAU OF GOVERNMENT LABORATORIES,
OFFICE OF THE SUPERINTENDENT OF LABORATORIES,
Manila, P. I., March 25, 1905.

SIR: I have the honor to transmit herewith and to recommend for publication articles entitled (1) Autocatalytic Decomposition of Silver Oxide, (2) Hydration in Solution, by Gilbert N. Lewis, Ph. D., Physical Chemist.

Very respectfully,

RICHARD P. STRONG,
*Director Biological Laboratory,
Acting Superintendent Government Laboratories.*

HON. DEAN C. WORCESTER,
Secretary of the Interior, Manila, P. I.



AUTOCATALYTIC DECOMPOSITION OF SILVER OXIDE.

By GILBERT N. LEWIS, Ph. D., *Physical Chemist.*

In the course of an investigation to determine the equilibrium pressure at a given temperature in the system $2\text{Ag}_2\text{O} = 4\text{Ag} + \text{O}_2$, a singular phenomenon appeared. The experiment consisted simply in heating silver oxide at a constant temperature of 335°C ., the stout glass tube which contained the oxide being connected with a manometer. After heating several hours the manometer gave no evidence that any decomposition had occurred. This occasioned some surprise, since 250°C . is frequently given as the temperature at which silver oxide begins to decompose. As I was about to stop the experiment in order to test the tightness of the joints I detected a slight deflection of the manometer. This increased considerably during the next hour, and I noticed that the greater the pressure became the greater became the rate of its increase, until finally the pressure had reached 20 atmospheres and was increasing at the astonishing rate of between 3 and 4 atmospheres per hour. At this point the cement joining the tube and the manometer began to give way and the experiment had to be discontinued. It had progressed far enough, however, to stimulate considerable curiosity as to the explanation of so unusual a behavior.

The gradual acceleration in the decomposition which was observed could only be attributed to one of the following causes: (1) The increasing pressure; (2) the increasing concentration of oxygen; (3) the accumulation of metallic silver; (4) some change in the silver oxide, such as the slow agglomeration of its grains. Of these four the first two were eliminated at once by a rough experiment carried on at atmospheric pressure, which showed the same phenomenon of accelerating decomposition. It seemed

worth while to study more carefully this decomposition under atmospheric pressure, and for this purpose the following apparatus and methods were devised:

EXPERIMENTAL METHOD.

The apparatus finally adopted for the experiments is sketched in fig. 1. For the thermostat a mixture of sodium and potassium nitrates was used, contained in a cylindrical vessel of enameled iron ("agate ware"), about 30 centimeters in diameter and 25 centimeters in height. (A in fig. 1.) This vessel rested on a tripod and was heated from below by two Bunsen burners. The heating efficiency and the constancy of the thermostat were surprisingly increased by a sheath of asbestos (B) surrounding the bath and projecting 10 or 15 centimeters below it. This sheath was separated about one-half centimeter from the side of the vessel by a number of corrugated brass strips not shown in the figure. An annular space was thus left between the asbestos and the bath through which the hot gases from the burners could pass freely and thus heat the thermostat from the sides as well as from below. The careful adjustment of this sheath seemed to be almost essential to the satisfactory operation of the thermostat.

The stirrer was made very simply without the use of solder, combining the ordinary method of stirring with the centrifugal, and it was so effective that the different parts of the bath never differed by more than one or two hundredths of a degree.

The temperature regulator was simply a large mercury thermometer made of a spiral of thin glass sealed to a vertical capillary (C). Into this capillary two fine platinum wires were sealed so that when the expansion of the mercury brought it into contact with the upper wire an electric current from a storage battery was made, which, passing through a telegraph instrument, shut off a thin rubber tube supplying gas to one of the burners.

This regulator was in fact the only part of the apparatus that caused the slightest inconvenience. The spiral being made of thin glass and holding nearly a kilogram of mercury was very fragile, and, being weakened further by the continued high temperature, broke several times and had to be replaced. If a regulator of the same type could be made of some suitable metal, which would also have the advantage, because of its high conductivity, of responding more rapidly to changes in the temperature, a very

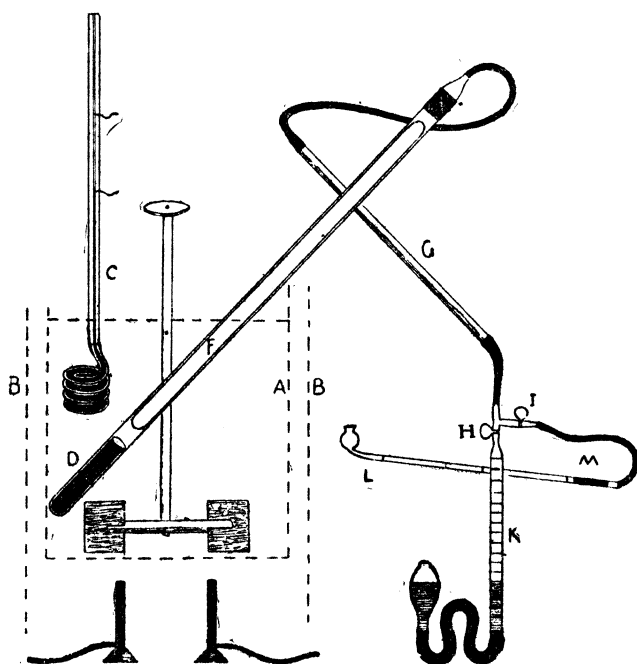


FIG. 1.

great constancy might be attained, for a thermostat working at this temperature has two great advantages over the common water thermostat—it is influenced very slightly by changes in the room temperature and there is no loss of heat by evaporation. It must, however, like all thermostats, be protected from drafts of air.

The mixture of potassium and sodium nitrates proved to be an ideal bath liquid. When pure it is as clear as water and as mobile. Well-annealed glass apparatus and thermometers may be plunged directly into the liquid again and again without breaking.

The vessel of enameled ware seemed to suffer no deterioration whatever, even after several months of contact with the molten salt.

The apparatus for containing the silver oxide and measuring its rate of decomposition is also sketched in fig. 1. The glass tube (D), about 1 meter long, was filled with carefully dried silver oxide to a height of about 10 centimeters, and the powder was shaken compactly into the end. This was covered with a thin layer of glass wool and the remainder of the tube was filled with a loose-fitting glass rod (F), the object of which was merely to diminish as far as possible all air space subjected to changes of temperature, and thus to avoid fluctuations in volume. The end of the tube containing the oxide was immersed deeply in the thermostat, and the other end was connected by rubber tubing to a long brass tube (G), in passing through which the evolved oxygen was cooled to the temperature of the room. The end of this brass tube was connected with a gas burette (K) and to the recorder (L). This latter was simply a glass tube about 2 millimeters in diameter marked off at such intervals that the volume from one mark to the next was exactly 1 cubic centimeter. A small column of water (M) served as an index. With stopcock H closed and I open the small water column advanced along the recording tube, and the time taken by the forward meniscus in moving from one mark to the next was read with a stop watch. When the reaction was very fast, the recording meniscus was allowed to run through several centimeters in order to permit a more accurate measurement of the time. Thus it was possible to measure accurately the rate of evolution of oxygen, whether 1 cubic centimeter in an hour or 1 cubic centimeter in ten seconds, the latter being the greatest velocity measured. After determining the reaction velocity the water indicator could be brought back to its initial position by cautiously opening the stopcock H. I was then closed and H

left open, thus allowing the gas to collect in the burette until the velocity was again measured. In this way the velocity at any moment, and the total volume of gas that had been evolved, could be measured independently. However, after the first few experiments, the burette was done away with and only the velocity was measured, as it was found that in the few cases where a knowledge of the total volume was desired it could be ascertained with sufficient accuracy from the time-velocity curve.

This simple apparatus gave complete satisfaction, cleanliness in the recording tube being the only precaution necessary for its success.

THE COURSE OF THE REACTION.

In the first experiment with the apparatus 4.4 grams of silver oxide was used, the temperature was 327.5° C., and the measurements of the reaction velocity were made for twenty-four hours at intervals of one-half to one hour. For several hours the decomposition was inappreciable; at the end of 10 hours the rate was 1 cubic centimeter of oxygen evolved per hour; after 13 hours, 1 cubic centimeter in 27 minutes; after 14 hours, 1 cubic centimeter in 18 minutes; after 16 hours, in 4 minutes; after 18 hours, in $1\frac{1}{2}$ minutes, and at this point the velocity was increasing rapidly. After 20 hours the rate was 1 cubic centimeter in 1 minute and rapidly falling, showing that between the last observation and this a point of maximum velocity had been reached. After $20\frac{1}{2}$ hours the rate of evolution was 1 cubic centimeter in 2 minutes; after 21 hours, 1 cubic centimeter in $3\frac{1}{2}$ minutes; after $21\frac{1}{2}$ hours, in 7 minutes, and before 24 hours had passed all action had ceased.

This experiment gave a general idea of the course of the reaction. At the beginning the velocity is very small, increasing more and more rapidly to a maximum, then falling—rapidly at first, later more slowly—until finally the reaction is complete. This decomposition has the general character of an explosion, and in fact it is nothing more or less than an explosion which is slow enough so that its velocity can be measured, and differing from the ordinary explosion only in that in the latter case a reaction progresses with accelerating velocity because of increasing temperature, due to the heat given off by the reaction, while the decomposition we are studying takes place at constant temperature and is in fact an endothermic reaction.

To find the cause of the acceleration in this case was the next problem. Two possible explanations were left. The phenomenon might be due to a gradual physical change in the silver oxide, such as to bring it into a more and more reactive condition, or it might be due to the presence of the silver produced in the reaction. The latter supposition could fortunately be tested directly by experiment, for if the silver formed by the reaction were a catalyzer, then unquestionably silver prepared in the same way and mixed with the oxide before the experiment would produce a similar effect. Therefore, the preceding experiment was repeated, using instead of the pure silver oxide a mixture of 5.5 grams of oxide and 0.1 gram of the powdered metallic silver obtained from the last experiment. These were rubbed together until very intimately mixed.

Noticeable decomposition began as soon as the mixture was put into the thermostat. The rate of evolution of oxygen after 2 hours was 1 cubic centimeter in 5 minutes; after 5 hours, in 3 minutes; after 7 hours, in $1\frac{1}{2}$ minutes. After about 8 hours the maximum of 1 cubic centimeter per minute was reached, and in 12 hours the reaction was over. In the previous experiment the reaction at the end of 12 hours was just beginning to have a measurable velocity. This difference between the two experiments seemed to point conclusively to catalytic action by the silver, yet it was not inconceivable that it might be due to some difference in the treatment of the two samples of silver oxide. In order to remove this doubt the following experiment was tried later under new conditions with a different preparation of silver oxide and at a different temperature:

Three portions of silver oxide were taken, each weighing 3.3 grams. To the first (A) 1.1 grams of silver powder was added, to the second (B) 0.55 of a gram of silver, and the third (C) was left pure. All three were subjected to precisely the same treatment of rubbing and stirring, and introduced in separate tubes simultaneously into the thermostat. At the end of three-quarters of an hour 1 cubic centimeter of gas was evolved from A in 72 seconds, from B in 85 seconds, and from C in 215 seconds; at the end of an hour from A in 42 seconds, from B in 56 seconds, and from C in 210 seconds. The velocity reached its maximum for A in 88 minutes, for B in 110 minutes, and for C in 160 minutes.

This experiment demonstrated the catalytic influence of the silver and showed that this influence increases with the quantity of silver. More precise quantitative results were not looked for, as it was assumed that the action of the decomposed silver would be dependent upon the degree of fineness, the intimacy of its mixture with the oxide, and possibly upon other conditions which could not be made entirely uniform. It seemed likely that a careful study of the form of the reaction curve for the pure oxide would yield more trustworthy information as to the law and mode of action of this catalysis.

A series of experiments was therefore carried out, similar to the one already described, but with more frequent and more accurate determinations of the velocity. A considerable number of such series was made at different temperatures, and of these I have chosen the four most complete and satisfactory for further discussion. These were made at 327.0°C. , 332.5°C. , 352.2°C. , and 353.3°C. , and may be designated by A, B, C, and D, respectively.

The results are represented in fig. 2, the reaction velocity being plotted vertically and the time horizontally. Instead of the time when the experiment began, the time of maximum velocity is taken as zero. Thus, the maxima of all the curves fall on the same vertical line. The velocity is expressed as the fraction of the whole quantity of oxide which is decomposed per second. This can, of course, be readily found from the rate of evolution of oxygen when the temperature and pressure and the weight of silver oxide are known. If x represents the fraction of the original oxide that has been decomposed, the velocity is $\frac{dx}{dt}$.

An inspection of these curves shows, as was to be expected, that the maximum velocity is greater and, the whole time of the decomposition less, the higher the temperature of the experiment. Further, we are struck by the great regularity of the curves and by their very evident similarity to one another. They appear to belong to a single family of curves such as may be represented algebraically by a single equation with one variable parameter. It seemed likely that if these curves were reduced to the same scale they might nearly coincide.

This was attempted by plotting each experiment with a different unit of time, so chosen as to make each maximum velocity equal

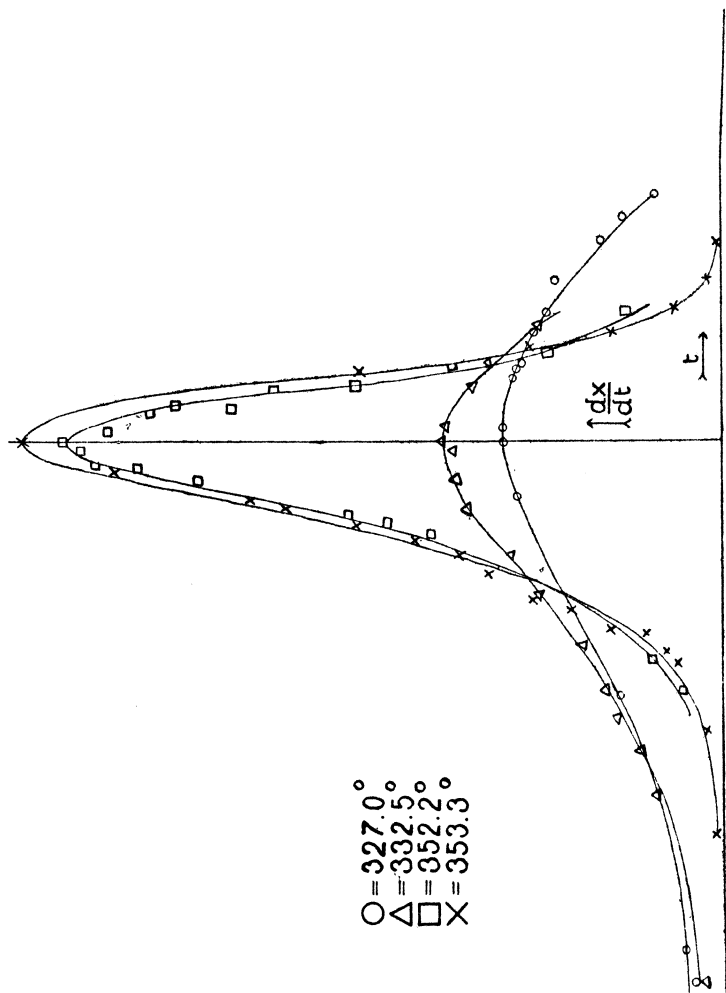


Fig. 2.

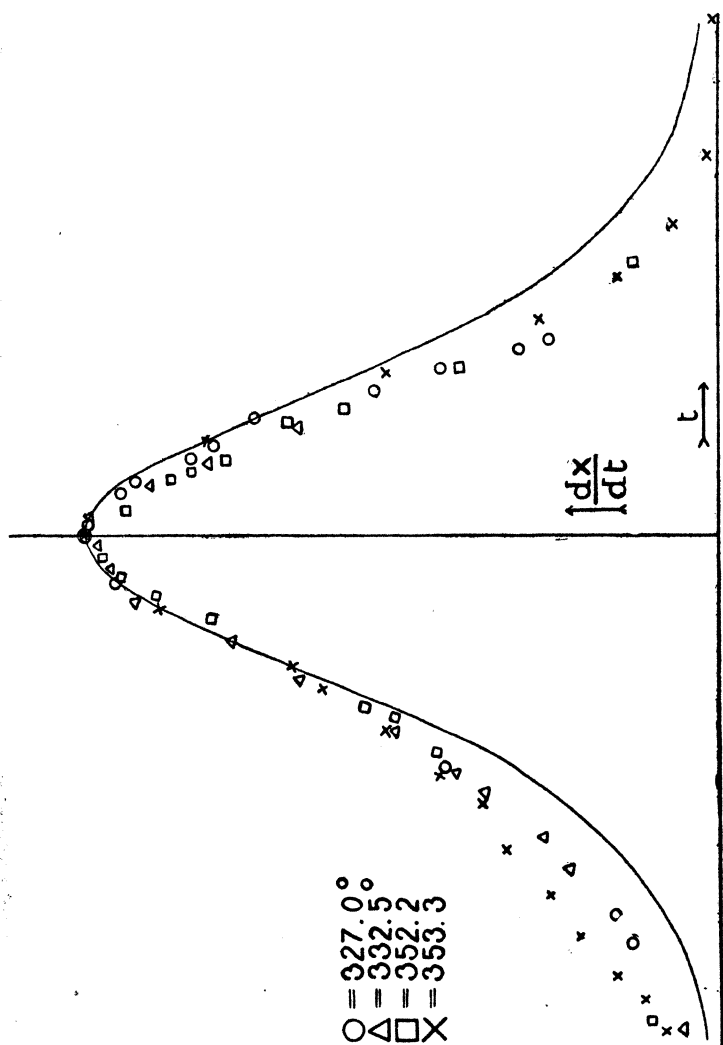
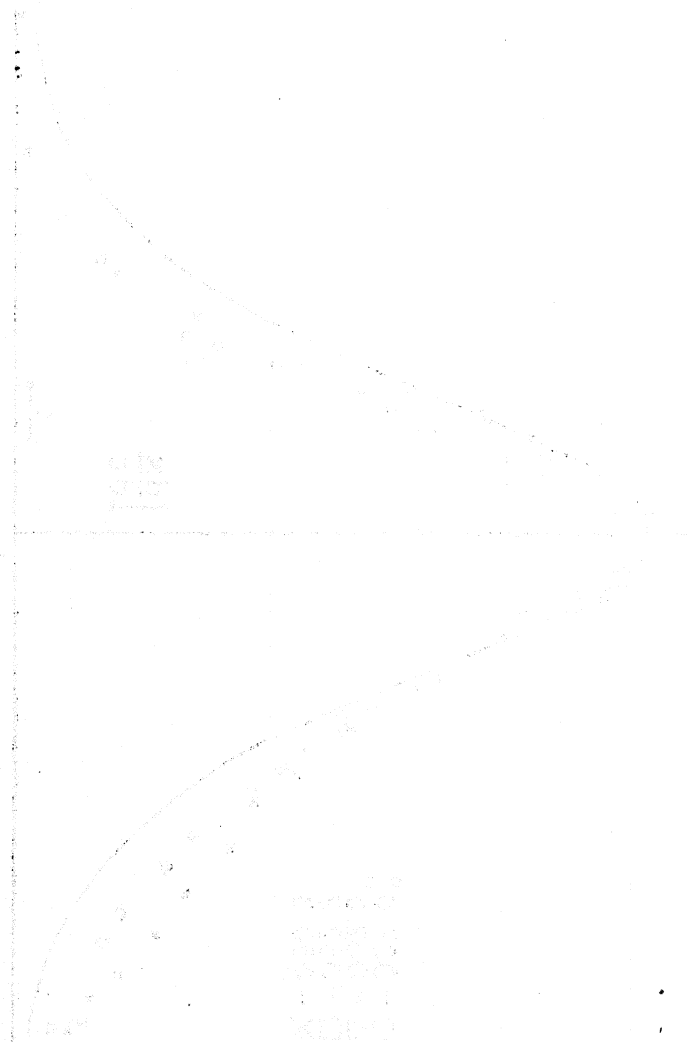


Fig. 3.



to unity, hence the unit of time in each case is the time which would be required for complete decomposition if the whole reaction progressed at a uniform rate equal to the maximum velocity. In other words, the units of time chosen are inversely proportional to the maximum velocities, which, therefore, in the new scale become numerically equal and fall on a single point.

The four curves thus plotted in fig. 3 come astonishingly near to coincidence; in fact, they do coincide within the limits of experimental error.

Among all the cases in which reaction velocity has been studied the present phenomenon occupies a wholly unique position. Exceedingly few autocatalytic reactions have been quantitatively investigated. In a homogeneous system the study of the reaction of oxalic acid and permanganate by Schilow¹ may be mentioned; in heterogeneous systems the study of the action of acids on sodium thiosulphate by Fousseureau² and the decomposition of hydrogen arsenide, hydrogen selenide, and hydrogen antimonide, respectively, by Cohen,³ Bodenstein,⁴ and Stock and Guttman.⁵ In all these cases in heterogeneous systems a reaction in a liquid or gaseous phase is catalyzed by a solid product. Bodenstein,⁶ recalculating the work of Stock and Guttman, points out the surprising simplicity and regularity of the decomposition studied by them. But how much more surprising it is that in our present case the decomposition of one solid is catalyzed even more regularly by the the presence of another solid with which, in the very nature of solid substances, it can not be in very intimate contact. The decomposition behaves, indeed, almost like a simple homogeneous reaction.

In a homogeneous catalytic reaction the simplest case is that in which, for a given volume, the reaction velocity is proportional to the quantity of the reacting substance and to the quantity of the catalyzer. Let us see how nearly the decomposition of silver oxide conforms to these conditions.

¹ *Ber. Chem. Ges.*, 36, 2735 (1903).

² *Ann. Chim. Phys.*, (6) 15, 533 (1888).

³ *Zeit. Phys. Chem.*, 25, 483 (1898).

⁴ *Zeit. Phys. Chem.*, 29, 429 (1899).

⁵ *Ber. Chem. Ges.*, 37, 901 (1904).

⁶ *Zeit. Phys. Chem.*, 49, 41 (1904).

If we assume that the velocity of reaction is proportional to the quantity of silver oxide and of silver, we may write the equation,

$$\frac{dx}{dt} = Kx(1-x) \quad (1)$$

Where $\frac{dx}{dt}$ measures the velocity, x is the fraction of oxide decomposed and is therefore proportional to the amount of silver. $1-x$ is the fraction remaining unchanged and is therefore proportional to the amount of silver oxide. K is a constant.

An inspection of the equation shows that it would be represented by a rising and falling curve, with a maximum of velocity at the point where just one-half the silver oxide is decomposed. In order to compare the assumptions we are making with our experimental results we must obtain the velocity as a function of t rather than of x . From equation 1, by integration, $\ln \frac{x}{1-x} = Kt + C$, where \ln stands for a natural logarithm and C is the integration constant. If we count t from the point of maximum velocity, then at that point $Kt = 0$. Also, since $x = (1-x)$, $\ln \frac{x}{1-x} = 0$, and therefore $C = 0$. Therefore our equation stands

$$\ln \frac{x}{1-x} = Kt, \quad \text{or } \frac{x}{1-x} = e^{Kt}, \quad \text{or } x = \frac{e^{Kt}}{1+e^{Kt}} \quad (2)$$

differentiating this equation

$$\frac{dx}{dt} = \frac{Ke^{Kt}}{(1+e^{Kt})^2} \quad (3)$$

This is the equation sought, and in order to plot its curve on a suitable scale for comparison with those of fig. 3 we must choose in this case also such a unit of time as to make the maximum velocity equal to unity. At this maximum, then, $\frac{dx}{dt} = 1$, but, as previously shown,

$$x = \frac{1}{2} \text{ and } 1-x = \frac{1}{2},$$

whence by equation 1,

$$1 = K \frac{1}{2} \frac{1}{2}, \text{ and } K = 4,$$

whence equation 3 becomes

$$\frac{dx}{dt} = \frac{4e^{4t}}{(1+e^{4t})^2}$$

The continuous curve shown in fig. 3 is obtained by plotting this equation. Its great similarity to the experimental curves is obvious. Still, it is not quite identical with them. The experimental curves all lie nearer to one another than they do to the theoretical, and all show a certain asymmetry which that does not. In the case of the experimental curves it is evident that the apex comes at a point where more than one-half of the silver oxide is decomposed. Still the theoretical and experimental curves fall much nearer together than was to have been predicted, and it is possible that the existing difference may be due to faults in the experimental method; thus, for example, it is not impossible that near the point of maximum velocity the reaction may take place so rapidly that heat can not be absorbed from the bath rapidly enough to maintain a constant temperature, a condition which would destroy the symmetry of the curve. Still it is hardly probable that this was the case, for if it had been there would have been a wide difference between the curves for the highest and the lowest temperatures, since at the latter the maximum velocity is only one-third or one-fourth as great as at the former.

THE STUDY OF DIFFERENT VARIETIES OF SILVER OXIDE.

In the experiments hitherto described the same silver oxide was used, namely, a preparation by Merck labeled "highest purity." When this was exhausted the experiments were continued with an oxide made by Eimer & Amend. However, it was soon found that with this substance no results could be obtained comparable with the preceding. The reaction velocity was far more rapid than with the old oxide. Thus, at 340° the maximum velocity was passed in less than an hour, and in three hours all action had ceased. Furthermore, the decomposition was irregular, so that under the same conditions inconstant results were obtained. This sample of oxide was therefore abandoned and another bottle of Merck's procured. This was of the same grade and bore the same label as that used in the previous experiments, but it too decomposed with great rapidity. Thus, the velocity at 352° reached a maximum in thirty-seven minutes and the reaction was over in three hours, whereas with the original sample at this temperature the maximum came at the end of four hours. The great irregularities shown by the Eimer & Amend samples, however, did not appear. Such irregularities most probably are due to lack of uniformity in the oxide.

The great difference in the rapidity of decomposition of different samples of oxide made it desirable to study the influence of the method of preparation of the oxide upon its decomposition. It seemed probable that the difference between samples was either due to varying quantities of impurities or to variations in the physical state; for example, in the fineness of division of the powder. Pure silver oxide was therefore prepared for study in three different ways. For all these preparations silver nitrate purified by several recrystallizations was used. In the first case sodium carbonate was added. The precipitated carbonate was washed repeatedly by decantation, the last washings occupying twenty-four hours each. It was then dried and heated at 240° for twenty-four hours to drive off as completely as possible the water and the carbon dioxide. The second and third preparations were made by treating the silver nitrate with a clear solution of barium hydroxide, in one case with both solutions at room temperature, in the other with both at 100° . All the solutions were very dilute and the reaction was carried on with the exclusion of carbon dioxide. The precipitates were carefully washed, and dried at 240° .

It was expected that the silver carbonate would yield a very finely divided oxide and, therefore, one that would rapidly decompose, but as a matter of fact it proved to react much more slowly than any which had previously been tried. The samples prepared with barium hydroxide decomposed more slowly still—more than four times as slowly as the oxide used in the earlier experiments. Contrary to expectation the oxide prepared in the cold decomposed rather more slowly than the other.

Therefore, it would appear from these few experiments that the rapid reaction of some of the samples was caused by the presence of impurities. Still, my experiments were hardly sufficient to make this conclusion certain, especially as certain observations led me to suspect that the rapidity and temperature of drying had some influence on the rate of decomposition. Unfortunately, however, my experiments at this point had to be brought to an abrupt close, and it is therefore necessary to leave this question open.

TEMPERATURE COEFFICIENT OF THE REACTION VELOCITY.

The influence of temperature on the reaction velocity may be found from the four experiments, the results of which are plotted in figs. 2 and 3, since they were all made with the same sample of oxide. We must choose for comparison the reaction velocities at corresponding points in the several experiments. The apices of the curves constitute such a series of corresponding points. The maximum velocities at the four temperatures, 327°, 332.5°, 352.2°, 353.3°, were, respectively, 0.0106, 0.0134, 0.0316, and 0.0335 per cent per second. If we plot the logarithms of these four numbers on the one hand and the corresponding temperatures on the other the resulting points lie almost precisely on a straight line whose slant is given by the equation

$$\frac{d \log_{10} v}{dT} = 0.0185,$$

Or, by the integrated form,

$$\log_{10} \frac{v_1}{v_2} = 0.0185 (T_1 - T_2).$$

It is customary to express the influence of temperature upon reaction velocity by means of the quotient of the velocity at one temperature divided by the velocity at a temperature 10° lower. This quotient can be easily found in the present case from the above equation. Since $T_1 - T_2 = 10$,

$$\frac{v_1}{v_2} = \log 0.185 = 1.53.$$

In other words, when the temperature rises 10° the velocity increases by about 50 per cent. This increase is less than that of most reactions, but corroborates the idea of Van't Hoff,¹ who writes concerning this quotient:

Bedeutend weniger als Verdoppelung zeigt nur die Zerlegung von Phosphor- und Arsenwasserstoff. Das hängt aber vielleicht mit der hohen Beobachtungstemperatur zusammen, denn in der grossen Mehrheit der bis jetzt beobachteten Fälle nimmt das Geschwindigkeitsverhältnis für 10° mit steigender Temperatur ab.

¹ *Vorlesungen ueber Theor. u. Phys. Chem.*

THE NATURE OF THE CATALYTIC ACTION.

At first sight the explanation of the catalytic action of the silver would seem to be like that which is sometimes offered for the development of a photographic plate, namely, that the silver as it is produced becomes supersaturated and finally reaches such a concentration as to stop the reaction except where silver is already present upon which it may deposit. If this explanation is correct the phenomenon we are studying closely resembles the simple process of crystallization from a supersaturated solution. In fact, I may point out that every case of such crystallization is a case of autocatalysis, and that here also the reaction velocity rises and falls as the crystallization continues—rises as the surface of the crystal increases, falls as the degree of supersaturation decreases.

Striking as the analogy is, it must be borne in mind that in this case we are dealing with the action of one solid upon another, and the great regularity of the reaction seems hard to reconcile with all the other facts known concerning reactions in solid phases.

As a result of other studies I have been inclined to entertain an entirely different explanation of the phenomenon. In the course of researches, some of which will shortly be published, I have been led to believe in the great importance to chemistry of the two following reactions:



These two reactions have frequently been discussed in connection with the theory of the nascent state, but little attention seems to have been paid to the immense importance of the *velocity* of these reactions in a large number of processes, such as the union of oxygen and hydrogen, combustions in general, reduction by hydrogen, spontaneous decomposition of oxydizing and reducing agents, and especially in the phenomenon of galvanic polarization. Here, however, this larger problem concerns us only as it offers a possible explanation of the autocatalysis of silver oxide. When we consider the probable mechanism of the decomposition it is evident that instead of the one reaction $2\text{Ag}_2\text{O} = 4\text{Ag} + \text{O}_2$ we may write with at least equal probability the two reactions $\text{Ag}_2\text{O} = 2\text{Ag} + \text{O}$ and $2\text{O} = \text{O}_2$. If in fact the decomposition takes place in these two stages the important question is, Which is the

reaction of which we are measuring the velocity?—that is, Which is the slower reaction?

We have many reasons to believe that the reaction $O_2 = 2O$ is an extraordinarily slow one. For example may be cited the inactivity of oxygen and the preponderating tendency in slow oxidation at ordinary temperatures for the oxygen to enter into the resulting compounds as the radical (O_2), forming the unstable peroxides. We may assume that to an extremely small extent oxygen gas is dissociated, that in ordinary O_2 there is a small concentration of O in equilibrium with it. If when the equilibrium is destroyed by removing some monatomic oxygen it is restored with great slowness, then it will be true also that if the equilibrium is destroyed in the opposite direction the recovery, according to the reaction $2O = O_2$, will likewise be slow.

It is not unlikely that this latter reaction is the one whose velocity we have been studying and that it is the one which is catalyzed by the presence of the silver. In fact, silver is known to catalyze many gaseous reactions.

The above line of reasoning would apply equally to other reactions in which oxygen is evolved. Let us consider two cases as different from this one as possible, namely, the decomposition of hydrogen peroxide and of potassium chlorate. Both of these reactions may be accelerated by catalyzers; the catalysis of the latter by manganese dioxide and of the former by manganese dioxide, platinum, and other substances is familiar to all chemists. If in these cases also we assume that the union of two atoms of oxygen is the reaction the slowness of which retards the decomposition, then this reaction is the one which is catalyzed by platinum and by manganese dioxide. Therefore, these substances, if our assumptions are correct, should aid the decomposition of silver oxide as silver does. We have thus the means of testing our suppositions by direct experiment.

Two tubes, each containing 5 grams of silver oxide, to one of which 0.25 gram of pure platinum black was added, were put into the thermostat simultaneously. The one containing platinum began to give off oxygen at once. At the end of two hours it was evolving 1 cubic centimeter in twelve seconds, while the other was evolving 1 cubic centimeter in ten minutes.

A similar experiment was made with another preparation of silver oxide, in which case the silver oxide containing platinum

was entirely decomposed in twenty-four hours and the other not until after three days. In a similar experiment manganese dioxide, which had been previously heated to redness, was used in place of the platinum and it also showed marked catalyzing power.

These results speak strongly in favor of the truth of the assumptions which we have made. It is true that catalysis of silver oxide and hydrogen peroxide by platinum may be specifically different, but let us consider a few of the reactions, where oxygen is a factor or a product, which are catalyzed by platinum; the combustion of gases such as hydrogen, methane, ammonia, vapor of methyl alcohol; the decomposition of oxidizing agents such as hydrogen peroxide; the electrochemical solution of oxygen at the cathode and its separation at the anode. Certainly there seems to be ground for believing that in all these cases, while several reactions occur together, an important, and in many cases the only, factor in determining the speed of the whole reaction, is the speed in one direction or the other of the intermediate reaction, $2O \rightleftharpoons O_2$, and that this reaction is catalyzed by platinum and by a number of other substances, of course as well in one direction as in the other.

At least we may conclude in regard to the decomposition of silver oxide that since there are substances besides silver which act as catalyzers the autocatalysis is not of the same nature as that of precipitation from a supersaturated solution, and further, that there is some ground for believing that the velocity which we measured is either that of the reaction $2O = O_2$ or that of the diffusion of the factors or products of this reaction, to or from the catalyzing substance.

We should expect the catalytic power of the silver to be proportional to the extent of its surface, while we have found it to be proportional to the amount of silver. But probably these two quantities are very nearly proportional since the silver is produced as a slightly cohesive mass which readily falls into a fine white powder. If the grains are of fairly uniform size the surface exposed is proportional to their number, or, in other words, to their mass.

SUMMARY.

A satisfactory thermostat for high temperatures is described, together with a method of measuring the velocity of decomposition of silver oxide.

This velocity of decomposition at constant temperature increases as the reaction proceeds, passes through a maximum, and falls gradually to zero.

The phenomenon is due to autocatalysis, and the catalyzing agent is metallic silver.

The reaction proceeds with great regularity and the curve of reaction velocity comes very close to the curve of the equation

$v = \frac{K e^{Kt}}{(1 + e^{Kt})^2}$, which is the equation of the simplest case of autocatalysis.

The influence of the purity and the method of preparation of the silver oxide upon its decomposition is discussed.

The temperature coefficient of the reaction velocity is determined.

Evidence, both experimental and theoretical, is offered in favor of a comprehensive theory of such catalytic action.



HYDRATION IN SOLUTION.

By GILBERT N. LEWIS, Ph. D., *Physical Chemist.*

The experiments which will be described in this paper, although of the simplest character, have so direct a bearing on the important question of hydration in solution as to merit a brief notice.

It is a remarkable fact that while inorganic reactions have been studied chiefly in aqueous solution, we have no knowledge as to whether, or to what extent, the solutes enter into chemical combination with the water. It is true we have many independent reasons for suspecting that such union occurs with a considerable number of salts, especially those which dissolve with the evolution of heat and which are noticeably hygroscopic—that is to say, which lower to an abnormal degree the vapor pressure of the solvent. However, no conclusive proof of such union has been found, nor any means of determining quantitatively what per cent of the solute molecules are combined or how many molecules of water unite with each.

The only attempt at such a quantitative determination of the extent of hydration has been made by Jones and Getman.¹ They base their calculations on the assumption that even in solutions as concentrated as three times molecular-normal there are no deviations from the laws of dilute solution, the apparent deviations being due to hydration, which without changing the total number of solute molecules changes the number of free solvent molecules.

Such an assumption lacks plausibility in any case, but especially as it leads the authors to a conclusion which is inconsistent with the fundamental principles of chemistry. This conclusion is that in many cases the degree of hydration increases with the concentration of the solute. Suppose that the hydration occurs according

¹ *Zeit. Phys. Chem.* 49, 385 (1904).

to the reaction, $S + n \text{H}_2\text{O} = S(\text{H}_2\text{O})_n$. According to the mass law, $\psi_1\psi_2^n = K\psi_3$, where ψ_1 and ψ_3 represent what is sometimes called the "active mass" of the unhydrated and hydrated solute, respectively, ψ_2 that of the water. ψ_1 and ψ_3 are nearly proportional respectively to the concentration of S and of $S(\text{H}_2\text{O})_n$, ψ_2 to the vapor pressure of water. Since the latter decreases with increasing concentration of the salt, ψ_1 must increase faster than ψ_3 —that is, the degree of hydration must decrease with increasing concentration. If instead of one a number of hydrates are formed, this same argument would apply to each reaction. The only case in which hydration could increase with the concentration would be the case in which polymerization accompanies hydration. But in the experiments of Jones and Getman there is no evidence of such polymerization, the presence of which would in any case invalidate their calculations.

Although we can not accept all the conclusions of these authors, nevertheless their experimental data, regarded as evidence in favor of the general idea of hydration, are of great value, and, while probably incapable of any such exact quantitative application as the authors have attempted, still serve to give us a very good idea of the probable relative hydration of different salts.

The method of Jones and Getman is not the only one which has been employed in attacking this problem, and the various methods all give evidence of the existence of hydration, and usually agree also as to which salts are to the highest degree hydrated. All these attempts have been brought together in an excellent monograph by Baur.¹

I wish to approach the subject of hydration from a different point of view, by a study of the colors of certain salts in solution, namely, chloride of cobalt and the chloride and bromide of copper. These substances have different colors when in concentrated and in dilute solution. Cobaltous chloride changes from purple to a clear red, cupric chloride from an olive green to blue, and cupric bromide from a dark brown through varying shades of brown and green to blue. These changes were in 1887 attributed by Wiedemann² to gradual hydration of the salts. However, this explanation has been succeeded by another, according to which the change of color is due to the electrolytic dissociation of the

¹ Ahrens Samml. Chem. Vorträge. 8, 456 (1903).

² Report Brit. Assoc. for 1887, p. 346.

salt, the undissociated molecules and the ions being supposed to have different colors. As far as one can judge by the eye, all the intermediate colors which occur during the dilution of these solutions in every case can be considered mixtures in different proportions of two colors. In the case of cobaltous chloride the two are blue and red, of cupric bromide yellowish brown and blue. The theory is that the undissociated cupric bromide, for example, is brown, the cupric ion blue. As the solution is diluted the degree of dissociation increases until finally all trace of brown disappears and the color is the pure blue of cupric ion. This theory is further borne out by the fact that the addition of a bromide, which would be expected to push back the dissociation of cupric bromide, does in fact turn a blue solution to green or even brown.

I was first led to distrust the adequacy of this explanation by a research of Prof. H. M. Goodwin, read before the Boston Physico-Chemical Club, and as far as I know not yet published, in which he showed, by a quantitative study of the absorption spectra of copper salts in solution, that the greatest change in color which occurs on dilution does not come where the change in dissociation is the greatest, but at a much higher concentration, and that in some cases little change in the absorption spectrum accompanies the further dilution of a solution which is still to a large extent undissociated.

These experiments force us to seek another explanation of the color change, and the simplest is that of Wiedemann previously mentioned, according to which the change of color is due to change in the degree of hydration. There is much evidence in favor of this view. Anhydrous cobalt compounds are in general blue—for example, the borate and the silicate. The solid chloride of cobalt changes from red to blue on losing its water of crystallization. Unquestionably hydration is almost universally accompanied by an evolution of heat, wherefore by the principle of Le Chatelier the degree of hydration in solution should decrease with increasing temperature, and in fact a red solution of cobaltous chloride turns blue on heating. According to the other theory this change of color would have to be attributed to an enormous diminution in electrolytic dissociation. The experiments of Isaachsen¹ render this improbable.

¹*Zeit. Phys. Chem.* 8, 145 (1891).

However, if we are to give up the theory that the phenomenon is due to ionization, how shall we explain the change of color when other chlorides are added to cupric and cobaltous chlorides and when other bromides are added to cupric bromide?

In order to find what the actual facts in the case are, solutions were prepared of a large number of acids and salts, comprising bromides, chlorides, nitrates, and sulphates, all of the same strength, namely, thrice molecular-normal. These were made up in a number of ways and care was taken only that they should not be in error by more than 1 per cent. To equal volumes of these solutions the same small quantity of cupric bromide was added. The resulting solutions ranged from blue to green, except in the cases of the four bromides used, in which the solutions were all of an olive brown. Similar experiments were tried with copper and cobalt chlorides, using all the solutions except the bromides. The cupric chloride was green in the chloride solutions, blue in all the others. The cobaltous chloride was a bluish red in the chlorides, a pure red in the others.

If the differences of color are due to differences in hydration, we should, at first thought, expect foreign salts to have no effect on the color, except as through their own hydration they might deprive the colored salt of the water combined with it. We should therefore expect that the strongest dehydrating agents would have the most effect on the color, rather than substances with a common ion. However, as a matter of fact, such hygroscopic substances as sulphuric acid and calcium nitrate seem to have little if any greater effect than other salts.

Let us examine the matter more closely, and suppose that during the dilution one or several reactions of the following type take place: $\text{CuBr}_2 + n\text{H}_2\text{O} = \text{CuBr}_2(\text{H}_2\text{O})_n = \text{Cu}^+(\text{H}_2\text{O})_n^+ + 2\bar{\text{Br}}$.

As a matter of fact, the color change may be due chiefly not to a change from the anhydrous salt to a hydrated one, but from one with less water to one with more, or the ions may exist in any degree of hydration, but whatever the actual reactions are, we may assume the above reaction merely for the sake of concreteness. Let us further assume that the brown color is due to the CuBr_2 and the blue to the $\text{CuBr}_2(\text{H}_2\text{O})_n$ and the $\text{Cu}^+(\text{H}_2\text{O})_n^+$.

Anything which would make the reactions run from right to left would cause the brown color to increase at the expense of the blue.

According to the equation there should be, with a given concentration of copper salt, two simple methods of bringing about such a displacement of equilibrium, namely, by increasing the concentration of the bromide ion and by decreasing the "active mass" of the water. The addition of any other bromide to a solution of cupric bromide would make the solution browner in both ways, for it would not only increase the concentration of the bromide ion but it would also decrease the "active mass" of the water, since it lowers the vapor pressure.

When salts other than bromides are added to the cupric bromide this second influence alone is at work and we find that a relatively slight change of color is produced. Indeed we should expect from the above equation that the first influence would be much the more powerful unless n is a very large number. The question is, What will the result be of adding to equal quantities of cupric bromide different solutions with the same concentration of bromide ion but with different vapor pressures? In order to answer this question the following experiment was made:

The same quantity of cupric bromide was added to 10 cubic centimeters of a thrice-normal solution of each of the following bromides: KBr, NH_4Br , NaBr, LiBr. In these solutions the concentrations of bromide ion are nearly alike, being somewhat greater in the case of KBr, somewhat less in the case of LiBr. If this were the only factor determining the color we should expect the solution in KBr to be the most brown, that in LiBr the least.

The facts are just the opposite. The NH_4Br and NaBr solutions have nearly the same color, that of KBr is less brown, while the LiBr solution is very much browner. In all these solutions the blue is so faint as compared with the brown that the relative brownness of the solutions can be found by means of a colorimeter. Columns of LiBr, NaBr, and KBr solutions, respectively 14, 18.5, and 20 millimeters thick, appeared equally brown.

These experiments were repeated several times, a different quantity of cupric bromide being used in each instance. The results were the same. A small change in the concentration of cupric bromide in any solution changes only the density of the color but not its character.

It is obvious that something influences the color besides the concentration of the bromide ion. When we examine the vapor pressures we find a very considerable difference in the four solu-

tions, sufficient to account in a most satisfactory manner for the observed color differences. As a measure of the depressions of the vapor pressure we may use the lowering of the freezing point. The data used in the following discussion are obtained from the work of Jones and Getman,¹ sometimes by means of extrapolation. When this extrapolation is carried over a considerable range the number is indicated as doubtful by the mark \pm .

The freezing-point depressions of the four bromide solutions are, approximately, KBr, 12° ; NH_4Br , probably between NaBr and KBr; NaBr, $13\frac{1}{2}^\circ$; LiBr, 19° .

Similar experiments were made with cupric chloride and solutions of the five chlorides, KCl, NH_4Cl , NaCl, LiCl, and HCl. Here the colors are not so pronounced as in the previous case. All the solutions are green. No difference could be detected in the first three, but the LiCl solution was decidedly greener and the HCl solution still more so. The freezing-point depressions are, respectively, 11.1° , 11.7° , 12.2° , 15.0° , and 18.1° .

Since solutions of the chlorides of the bivalent metals have much lower vapor pressures than those of the univalent ones, it was expected that they would have a much greater influence on the color. SrCl_2 , CaCl_2 , MgCl_2 , BeCl_2 were used. The solutions were in fact much greener than in the preceding case, having an olive tint. They arranged themselves by color in the order given, the last being greenest, and between each solution and the next there was a very marked difference in color. The freezing-point depressions are, approximately, SrCl_2 , $30^\circ \pm$; CaCl_2 , 40° ; MgCl_2 , $48^\circ \pm$; and BeCl_2 , unknown. Similar experiments were made with one and one-half molecular-normal solutions of these substances, and BaCl_2 was added to the list. Here the color differences were slight but the solutions could be repeatedly arranged by color in the above order both by myself and by others, BaCl_2 assuming its proper place before SrCl_2 . The freezing-point depressions are, approximately, BaCl_2 , $9^\circ \pm$; SrCl_2 , 10° ; CaCl_2 , 11° ; MgCl_2 , 12° .

Of course these one and one-half normal solutions, on account of less dissociation, have a smaller concentration of chloride ion than the thrice-normal solutions of the chlorides of the first group, but the $1\frac{1}{2}n$ BeCl_2 had the same color as the $3n$ KCl.

Finally aluminum chloride, $3n$, was tried. As was to be

¹l. c. and *Zeit. Phys. Chem.* 46, 244 (1903).

predicted from its great freezing-point depression, which is at least 90° , it gave a deep olive-brown color.

All these experiments were repeated, using cobaltous chloride in place of cupric. The color differences here are less marked. The solutions of the chlorides of the first group all had practically the same red color with a tinge of blue. But in the second group the solutions were a more decided purple and arranged themselves in the same order as before—that is, BeCl_2 gave the solution with most blue in it. AlCl_3 gave a deep purple, and a four-times-normal solution of AlCl_3 gave a pure blue.

All these facts speak for the truth of the above explanation of the color changes, and give strong evidence of the hydration of the three substances CoCl_2 , CuCl_2 , and CuBr_2 . It may be remarked that these substances, according to the work of Biltz,¹ give unusually large depressions of the freezing point.

I believe that a quantitative study of these color changes by means of a spectro-radiometer might throw a great deal of light on the whole question of hydration, although any attempt to determine the formulas and the amounts of hydrates in solution is rendered difficult by the probability of the simultaneous existence as a rule of several different hydrates in each solution.

¹ *Zeit. Phys. Chem.* 40, 198 (1902).



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(Continued from second page of cover.)

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